A CONFORMAL OXIDATION-RESISTANT, PLASMA-POLYMERIZED COATING

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ABSTRACT

A comparative study was made of the surface recession (etching) of thin films of plasma-polymerized tetrafluoroethylene (PPTFE), polytetrafluoroethylene (PTFE), and ion-beam sputter deposited polytetrafluoroethylene (SPTFE) exposed to ground-state atomic oxygen [$O(^3P)$)] downstream from a nonequilibrium radio-frequency O_2 plasma. At 22°C, the etch rates for PTFE, SPTFE, and PPTFE were in the ratio of 8.7:1.8:1.0. A thin, conformal coating of PPTFE (etch rate of 0.3 nm/h at 22°C) was found to protect an underlying cast film of a reactive polymer, cis-1,4-polybutadiene, against $O(^3P)$ attack for the time required to fully etch away the PPTFE coating. From ESCA analysis, PTFE exhibited only minor surface oxidation (uptake of 0.5 atom % O) upon etching, its F/C ratio decreasing slightly from 2.00 to 1.97; PPTFE exhibited considerable surface oxidation (uptake of 5.9 atom % O) and a decrease in F/C ratio from 1.30 to 1.23; and SPTFE exhibited a surface oxidation (uptake of 2.2 atom % O) intermediate betweeen those of PTFE and PPTFE, with a decrease in F/C ratio from 1.73 to 1.67. A plasma-polymerized fluorocarbon coating such as PPTFE might be useful for space applications to protect polymers that are vulnerable to oxidation or degradation by oxygen atoms.

INTRODUCTION

Considerable interest exists in the surface recession (etching) of polymers exposed to ground-state atomic oxygen [$O(^3P)$] in low Earth orbital environment, and some effort has been devoted to seeking protective coatings for space applications (1). Previously, we reported that polybutadienes and related unsaturated hydrocarbon polymers are quite reactive towards $O(^3P)$ generated by a radio-frequency glow discharge in O_2, the etch rates being dependent upon polymer structure (2). Since Teflon (polytetra-fluoroethylene, PTFE) was reported to be resistant to $O(^3P)$-induced etching in the space environment, it was reasonable to expect that plasma-polymerized tetrafluoroethylene (PPTFE) -- a highly branched and crosslinked polymer (3) with a fluorine/carbon ratio of 1.3-1.4 in contrast to 2.0 for the linear PTFE -- would also be resistant. Indeed, since crosslinked natural rubber had been reported to be much more resistant to O_2 plasma etching than the corresponding uncrosslinked polyisoprene (4), there was the possibility that PPTFE could be even more resistant than PTFE. Thus, if PPTFE films, which are easily deposited on various substrates, could be shown to be especially resistant to $O(^3P)$ attack, they might be useful as protective coatings for vulnerable polymers deployed in space. This paper describes the $O(^3P)$-induced etching of PPTFE, PTFE and an ion-beam sputter-deposited PTFE (SPTFE), using ESCA to follow surface structural changes produced in these polymers. Thin films of PPTFE deposited onto cis-1,4-polybutadiene (CB) are shown to protect the latter polymer against $O(^3P)$ attack.

EXPERIMENTAL

PTFE film (25-μm thick) was obtained from Chemical Fabrics Corp., West Palm Beach, FL. A 533-nm film of SPTFE (on a silicon substrate) was kindly supplied by Bruce A. Banks, NASA Lewis Research Center, Cleveland, OH. Tetrafluoroethylene monomer (TFE) inhibited with d-limonene (SCM Specialty Chemicals, Gainesville, FL) was used without further purification to prepare PPTFE. PPTFE films were deposited on the polished surfaces of small square sections (1.42 cm^2) of silicon cut from an Si wafer, using the plasma polymerization reactor described previously (5). The following conditions were used for PPTFE deposition:

Power: 10 W at 13.56 MHz
TFE flow rate: 0.5 cm^3 (STP)/min
Pressure: 76 Pa (0.57 torr), discharge off
Deposition rate: 0.066 nm/s

The thickness of the PPTFE films (on Si), before and after etching, was measured with an ellipsometer. The density, determined from thickness and weight-gain measurements on Si substrates of known area, was

2.3 ± 0.1 g/cm^3. The etching of PPTFE, measured in nm, was expressed as mg/cm^2, after multiplying the thinning (in cm) by the density (in mg/cm^3). The etching of SPTFE was similarly followed by ellipsometry. Weight loss in the PTFE films (disks cut to area of 2.54 cm^2) was measured on an automatic electrobalance and likewise expressed as mg/cm^2.

The O(^{3}P) reactor (2) is shown in Figure 1. The O$_2$ and O atom flow rates (the latter obtained by titration with NO$_2$) were 3.9 and 1.4 cm^3 (STP)/min, respectively, and O atom partial pressure was 0.17 torr
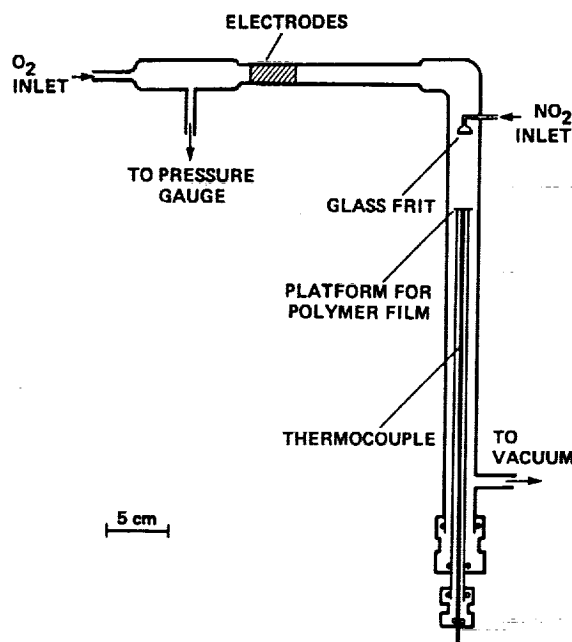

Figure 1. Apparatus for exposure of polymer films to O(^{3}P).

at the NO$_2$ titration port. Temperature was measured with a thermocouple having a junction located beneath the sample platform. ESCA analysis was performed, using Teflon tape as a standard, and the binding energies of PPTFE and SPTFE were referenced for the single F_{1s} peak of $\backsim$CF-/-CF$_2$-/-CF$_3$ at 689.2 eV.

To demonstrate the protectiveness imparted by PPTFE coatings, an Si substrate and a CB film (cast onto a glass cover slip) were simultaneously exposed to TFE for the same length of time in the plasma polymerization reactor. The resulting PPTFE coatings -- assumed to have the same thickness on Si and on CB -- were each subjected to O(^{3}P) for various periods of time. Thickness measurements were made on the former coating until the PPTFE was completely etched away, while weight-loss measurements were made on the latter coating to record the onset and subsequent etching of CB.

RESULTS AND DISCUSSION

In our original paper (2) we presented kinetic plots for O(^{3}P)-induced surface recession, or etching, of PPTFE and PTFE films at temperatures ranging from 22°C to 177°C. In contrast to PTFE, which is stable throughout this temperature range, PPTFE undergoes a thermally induced thinning in the absence of O atoms, which becomes increasingly significant as the temperature exceeds ca. 50°C. For the purposes of this presentation, we shall confine our attention to kinetic data obtained at 22°C; at this temperature, the etch rate for PTFE (5.3×10^{-4} mg/cm^2 h) was found to be 8.7 times that of PPTFE (6.1×10^{-5} mg/cm^2 h). That PPTFE has a higher resistance than PTFE to O-atom attack at ambient temperature is accounted for on the basis that the former polymer has a crosslinked structure (3) while the latter has a linear structure. SPTFE, on the other hand, had an etch rate at 22°C (1.1×10^{-4} mg/cm^2 h) that was 1.8 times that of PPTFE but only 0.21 times that of PTFE. That SPTFE had an etch rate closer to that of PPTFE than to that of PTFE is not surprising since ion-beam sputtering of PTFE involves breakdown of the latter's linear polymer

structure and reconstitution elsewhere of a polymer network from the PTFE fragments. Based on ESCA results given below, SPTFE has a structure that is less crosslinked than PPTFE and contains short sequences of CF_2 groups. At any rate, the lower etch rate for SPTFE compared to PTFE reinforces the viewpoint that crosslinking enhances resistance to $O(^3P)$-induced etching of an otherwise linear polymer.

The protectiveness of a very thin PPTFE coating against $O(^3P)$-induced etching at ambient temperature is illustrated in Figure 2 by means of two PPTFE coatings having the same initial thickness (16.8 nm) -- one deposited onto an Si substrate (for following decrease in thickness), the other onto a CB
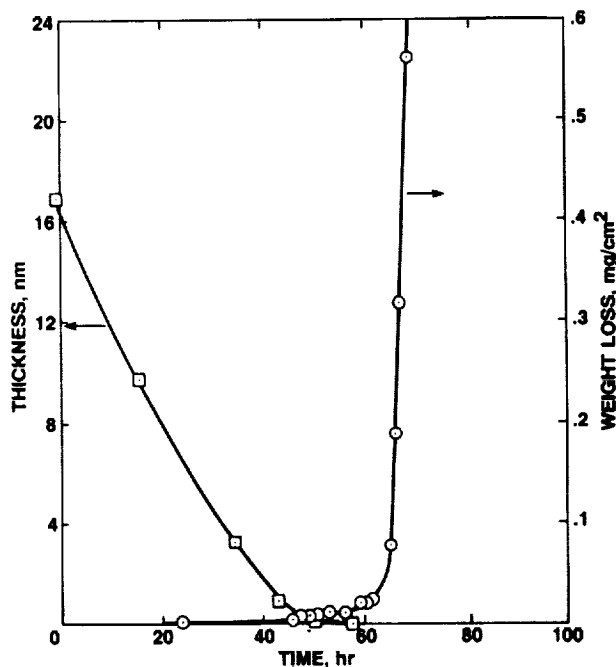

Figure 2. Protective effect imparted by a PPTFE coating against $O(^3P)$ attack at 22°C: (□) thinning of a PPTFE coating on Si substrate; (○) weight loss in a PPTFE coating on a CB film cast on a glass cover slip. Both PPTFE coatings had the same initial thickness (16.8 nm).

film cast on a glass cover slip (for following weight loss). As may be seen, the onset of significant weight loss in the PPTFE/CB sample occurs only after a time interval (ca. 50-60 h) required for the PPTFE coating to be nearly completely etched away (the weight of the PPTFE coating being immeasurable in this sample). This is demonstrated by the fact that the PPTFE/Si sample reaches a negligible thickness (0.2 nm) after this same time interval. In fact, the "breakthrough" point is in good agreement with the predicted value of about 62 h, given an etch rate for PPTFE of 0.27 nm/h ($\equiv 6.1 \times 10^{-5}$ mg/cm^2 h) at 22°C. Moreover, the sharp rise in the weight-loss curve of PPTFE/CB, subsequent to the disappearance of the PPTFE coating, yields an etch rate for CB of 0.18 mg/cm^2 h, which agrees quite well with the previously reported etch rate of 0.13 mg/cm^2 h for CB in the same $O(^3P)$ reactor (2). The near constant weight of the PPTFE/CB sample prior to total disappearance of the PPTFE coating indicates that O atoms do not diffuse into PPTFE to any significant extent. At the same time, it implies that the PPTFE coating is *conformal* and free of pinholes.

The C_{1s} and O_{1s} regions of the ESCA spectra of PPTFE films before and after etching at 22°C are shown in Figures 3 and 4. The analytical data are summarized in Table 1, where the estimated accuracy of each deconvoluted peak area (given in parentheses) is ±5% of its given value, while the estimated accuracy of each F/C ratio is ±2% of its given value. Since the F_{1s} regions were unchanged and, moreover, resembled the single intense peak at 689.2 eV (-CF$_x$) in the ESCA spectra of PPTFE (6) or of Teflon, there is no need to show them here. The C_{1s} spectrum of unetched PPTFE is very similar to the spectra of polymers
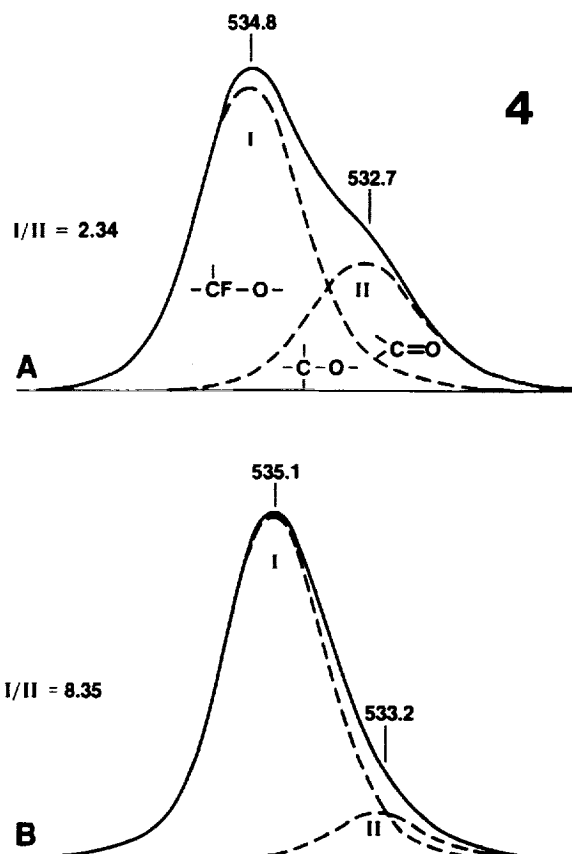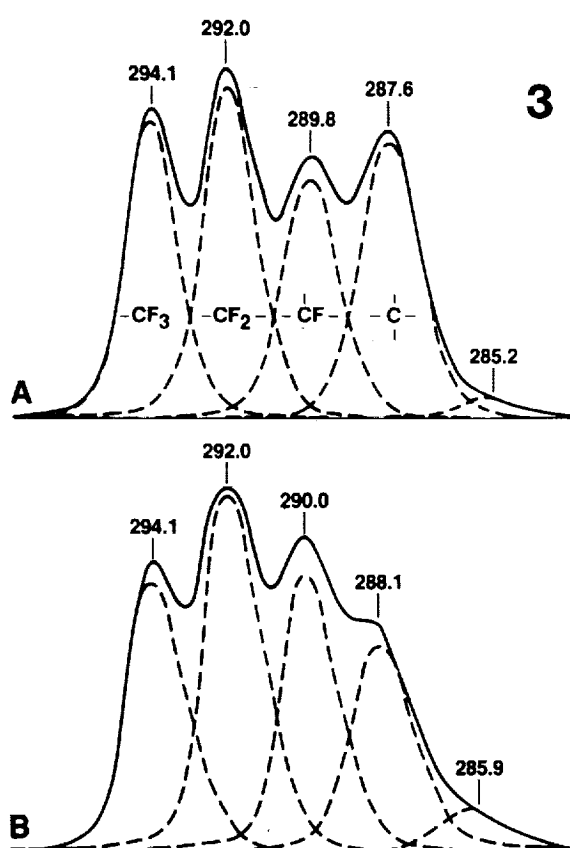
Figure 3. C_{1s} regions of ESCA spectra of PPTFE before (A) and after (B) $O(^3P)$-induced etching. Assignments of peaks under B are the same as those under A, except for additional groups indicated in footnotes of Table 1. Binding energies in this and the following figures are given in eV units.

Figure 4. O_{1s} regions of ESCA spectra of PPTFE before (A) and after (B) $O(^3P)$-induced etching. Spectra are not to scale; area under B corresponds to 8.4 times area under A.

TABLE 1

Atom (and Peak Area) % Distribution in ESCA Spectra of PPTFE[a]

Condition	$-CF_3$	$-CF_2-$	$-\overset{\mid}{C}F-$	$-\overset{\mid}{\underset{\mid}{C}}-$	$-CH_2-$	$-\overset{\mid}{C}F-O-$	$\overset{\diagdown}{C}{=}O$	$-CF_2-$	F/C
	C1s peaks					O1s peaks		F1s peak	
Unetched	9.9	11.9	9.3	11.3	0.8	0.6	0.2[b]	56.0	1.30
	(23.0	27.6	21.5	26.2	1.7)	(70.1	29.9)	(100.0)	
Etched	9.5[c]	13.1[d]	9.8[e]	8.1[e,f]	1.4[f]	6.0	0.7[b]	51.4	1.23
	(22.6	31.2	23.5	19.3	3.4)	(89.3	10.7)	(100.0)	

[a]Extent of etching at 22°C: ~ 9.5 nm.
[b]May include some $\overset{\diagdown}{C}-O-$.
[c]May include some $-CF_2-O-$.
[d]May include some $-\overset{\mid}{C}F-O-$.
[e]May include some $\overset{\diagdown}{C}{=}O$.
[f]May include some $\overset{\diagdown}{C}-O-$.

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obtained by various workers (6,7) from in-glow plasma polymerization of TFE in showing the same four prominent peaks with roughly the same relative intensities. However, these C_{1s} spectra differ from that of a PPTFE produced in nonglow regions (8), which approaches that of ordinary PTFE with its single $-CF_2-$ peak. There is universal agreement on the PPTFE assignments (6,7,9) shown in Figure 3(A), and the weak peak around 285 eV signifies a small amount of hydrocarbon contamination (7). To the extent that oxidation of the PPTFE surface occurs on exposure to $O(^3P)$, the various C_{1s} peaks in Figure 3(B) contain, besides the functional groups indicated in Figure 3(A), unknown amounts of C atoms attached to O atoms: $-CF_2-O-$ (294.1) and $-CF-O-$ (292.0 eV), as well as C atoms in $>C=O$ (288.1-288.9) and $>C-O-$ (286.7-287.5 eV) (see footnotes in Table 1). In addition, the ESCA spectra in Figure 3 are assumed to contain an undetermined amount of carbon atoms attached to double bonds (as in $=C<$, $=CF-$, or $=CF_2$ unsaturation (7)), which could comprise some 20% of the total carbon content in the unetched PPTFE (10); however, their exact locations under the various peaks cannot be specified. Hence, the data in Table 1 have only semi-quantitative significance, but they do point to a small decrease in the F/C ratio for PPTFE from 1.30 to 1.23 as a result of oxidative etching. It should be noted that these F/C ratios were determined by dividing the area under the F_{1s} peak by the total area under the five C_{1s} peaks (shown in Fig. 3), and adjusting the number by a sensitivity factor which acounts for the different cross sections for photoionization of F and C atoms. Another method, which involves calculating the F/C ratio from the percentage of each group present in the C_{1s} region and which is less reliable, typically yields F/C ratios higher by 0.2-0.4 than those calculated by the former method. As may be inferred from the data in Table 1, it is difficult to offer a detailed picture of the chemical changes occurring in the surface of the PPTFE film as it undergoes $O(^3P)$-induced etching; however, an essentially stationary state in surface composition is established as fresh surface is being regenerated even as the surface is being etched away.

PTFE, in contrast to PPTFE, showed very little oxygen uptake on exposure to $O(^3P)$, despite a more rapid rate of etching at 22°C: the ESCA spectrum for a film of PTFE etched to the extent of 0.4 μm showed only 0.47 atom % O (with an F/C ratio of 1.97), while the spectrum of the unetched PTFE (F/C = 2.00) showed no oxygen at all. The C_{1s} and F_{1s} spectra of PTFE before and after etching appeared unchanged, each exhibiting single peaks at 292.2 and 689.2 eV, respectively; hence the spectra were omitted here. Likewise, the O_{1s} spectrum of etched PTFE, which showed only a single peak at 532.3 eV $(>C=O)$, was also omitted.

The C_{1s} and O_{1s} spectra of SPTFE before and after etching at 22°C are shown in Figures 5 and 6, and the analytical data are summarized in Table 2. Here again, there was no need to show the corresponding F_{1s} spectra for SPTFE, since they each possessed but a single peak at 689.2 eV, in common with the F_{1s} spectra of PTFE and PPTFE. It is obvious from Figure 5 that the C_{1s} spectra of the unetched and etched SPTFE each have the appearance of a composite of the corresponding spectra of PTFE (with a single $-CF_2-$ peak at 292.0 eV) and of PPTFE (with its four prominent peaks), the latter two polymers *seeming* to be present in the approximate ratio of 4-5:1. This suggests that our SPTFE is considerably less crosslinked than the highly crosslinked PPTFE.

Since the changes observed in the C_{1s} spectra of PPTFE as a result of $O(^3P)$-induced etching (Fig. 3) are not dramatic, and since no changes were observed in the C_{1s} spectra of PTFE (as mentioned earlier), it is not surprising that the C_{1s} spectral changes in SPTFE (Fig. 5) upon etching are rather slight. However, there is an interesting difference between the O_{1s} spectra of SPTFE and PPTFE: whereas the ratio of areas of the two peaks I and II in Figure 4 increases considerably from 2.34 to 8.35, the corresponding ratio in Figure 6 decreases slightly from 1.53 to 1.39. This difference is likely due to SPTFE having a structure that is some 75-80% like that of PTFE and some 20-25% like that of PPTFE. Thus, for an oxygen uptake in SPTFE of 2.2 atom % (i.e., 2.7-0.5 atom % in Table 2), about 0.9/2.2, or 40%, of the oxidation presumably occurs at PTFE segments to produce the peak at 532.9 eV [Fig. 6(B)], given the prior observation that etched PTFE showed a single O_{1s} peak around 532.3 eV; the remaining 60% of the oxidation can be considered to occur at PPTFE branch points and/or crosslinks to produce the peak at 535.0 eV, given the dominance of the 535.1-eV peak in the O_{1s} spectrum of etched PPTFE [Fig. 4(B)]. Reflecting the mixed PTFE/PPTFE structure of SPTFE, it is worth recalling that the O uptakes in PPTFE, SPTFE, and PTFE -- after sufficient etching time to reach "equilibrium" oxidized surfaces -- were 5.9, 2.2 and ≈ 0.5 atom % O, respectively. Again, our SPTFE, with an initial F/C ratio of 1.73, had an etch rate that was about 2/9 of that of PTFE (with an F/C ratio of 2.0) and about twice that of PPTFE (with an initial F/C ratio of 1.30).
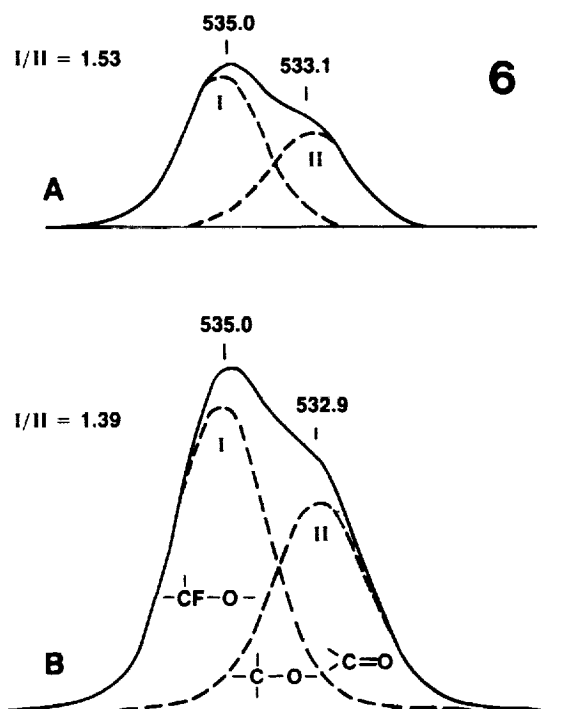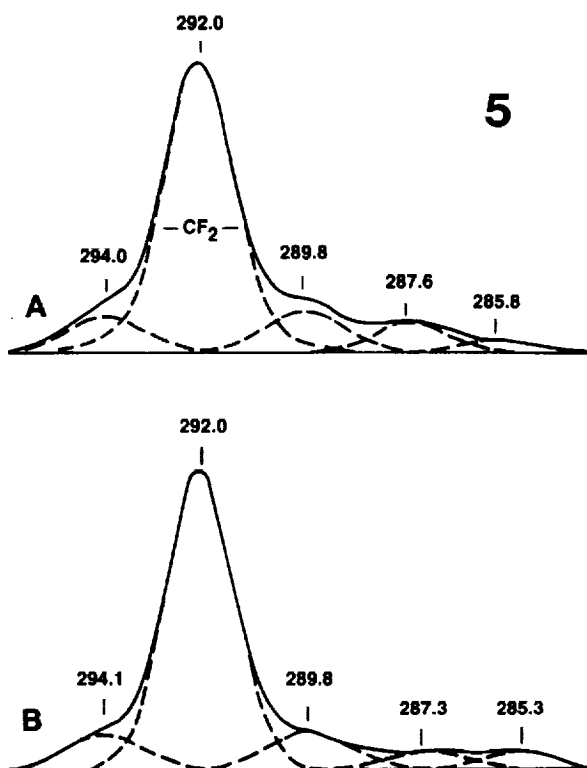
Figure 5. C_{1s} regions of ESCA spectra of SPTFE before (A) and after (B) O(^{3}P)-induced etching. Assignments of peaks under A and B are the same as those indicated in Figures 3(A) and 3(B).

Figure 6. O_{1s} regions of ESCA spectra of SPTFE before (A) and after (B) O(^{3}P)-induced etching. Spectra are not to scale; area under B corresponds to 5.4 times area under A.

TABLE 2

Atom (and Peak Area) % Distribution in ESCA Spectra of SPTFE[a]

Condition	C_{1s} peaks					O_{1s} peaks		F_{1s} peak	
	$-CF_3$	$-CF_2-$	$-\overset{\shortmid}{C}F-$	$-\overset{\shortmid}{\underset{\shortmid}{C}}-$	$-CH_2-$	$-\overset{\shortmid}{C}F-O-$	$\searrow C=O$	$-CF_2-$	F/C
Unetched	3.2	25.4	4.1	2.8	1.0	0.3	0.2	63.0	1.73
	(8.7	69.8	11.4	7.5	2.6)	(60.4	39.6)	(100.0)	
Etched	3.1[b]	26.4[c]	3.6[d]	1.8[d,e]	1.6[e]	1.6	1.1[f]	60.8	1.67
	(8.6	72.1	9.8	5.0	4.5)	(58.1	41.9)	(100.0)	

[a] Extent of etching at 22°C: ~ 48 nm.

[b] May include some $-CF_2-O-$.

[c] May include some $-\overset{\shortmid}{C}F-O-$.

[d] May include some $\searrow C=O$.

[e] May include some $\searrow C-O-$.

[f] May include some $\searrow C-O-$.

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